(16)

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **07-085874**
(43)Date of publication of application : 31.03.1995

(51)Int.Cl. **H01M 4/86**
H01M 4/88
H01M 4/92

(21)Application number : **05-229343**
(22)Date of filing : **16.09.1993**

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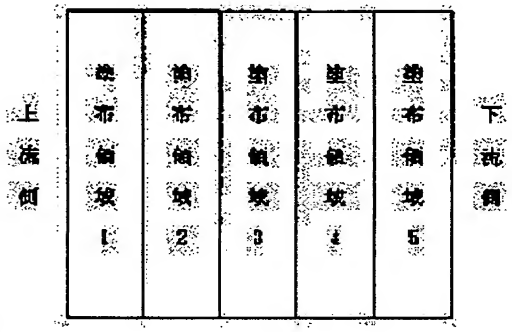
(54) FUEL ELECTRODE FOR FUEL CELL

(57)Abstract:
PURPOSE: To protect an electrode from the contamination of carbon monoxide in the downstream of the fuel gas, which includes carbon monoxide.
CONSTITUTION: A catalyst bed formed so that carrying quantity of platinum fine grains as catalyst is increased step by step from the upstream to the downstream of the fuel gas or one formed so that grain diameter of platinum fine grains are reduced step by step, is used, or in platinum-ruthenium alloy catalyst, a catalyst bed is formed so that quantity of ruthenium included in the catalyst bed is increased step by step from the upstream to the downstream of the fuel gas. Even in the case where density of carbon monoxide is relatively raised in the downstream of the fuel gas, hydrogen in the fuel gas is easy to be adsorbed by platinum, and corrosion of the electrode is not generated to stabilize a lifetime of the electrode for a long time.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]
[Claim 1] The fuel electrode of the fuel cell characterized by being the fuel electrode of the fuel cell which consists of a carbon base material and a catalyst bed which has the catalyst which supported the platinum particle to carbon black, continuing throughout resulting [from the upstream of the fuel gas supplied to this electrode] in the downstream, and forming the catalyst bed which carried out the sequential increment of the surface area of the platinum particle per electrode unit area gradually.
[Claim 2] It is the fuel electrode of the fuel cell characterized by performing the increment in the surface area of a platinum particle by increasing the amount of support gradually in a fuel electrode according to claim 1.
[Claim 3] It is the fuel electrode of the fuel cell characterized by performing the increment in the surface area of a platinum particle by making the particle size small gradually in a fuel electrode according to claim 1.
[Claim 4] The fuel electrode of the fuel cell characterized by being the fuel electrode of the fuel cell which consists of a carbon base material and a catalyst bed which has the catalyst which supported the platinum alloy particle to carbon black, continuing throughout resulting [from the upstream of the fuel gas supplied to this electrode] in the downstream, and forming the catalyst bed which carried out the sequential increment of the content of platinum and the element to alloy gradually.
[Claim 5] The fuel electrode of the fuel cell characterized by using a ruthenium in a fuel electrode according to claim 4 as platinum and an element to alloy.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the fuel electrode of the fuel cell which used the catalyst of a platinum system.
[0002]
[Description of the Prior Art] What usually reformed the original fuel of hydrocarbon systems, such as natural gas, from the economically disadvantageous thing in the gas which was rich in hydrogen content is being used for using hydrogen as fuel gas of a fuel cell as fuel gas. Impurities other than hydrogen gas, such as a carbon dioxide or a carbon monoxide, are contained in such reformed gas.
[0003] On the other hand, in the phosphoric acid form fuel cell and solid-state giant-molecule form fuel cell which are comparatively operated at low temperature, the platinum catalyst or platinum alloy catalyst which supported platinum or a platinum alloy is used for platinum black or carbon support by the electrode. It is known that this carbon monoxide adsorbs, polarization in a fuel electrode becomes large, the generated voltage of a fuel cell falls as a result, and a generated voltage will fall extremely especially when the operating temperature of a fuel cell is low if the carbon monoxide contains these electrode catalysts in fuel gas.
[0004] then , use the platinum-ruthenium alloy catalyst which cannot receive poisoning of a carbon monoxide easily as a catalyst which he be try to maintain the carbon monoxide concentration in fuel gas at extent which do not affect the engine performance of a cell , and be use for a fuel electrode in a cell proper be perform by the present condition remove a carbon monoxide to the reformer which reform a original fuel in the gas which be rich in hydrogen content , or give the function of oxidize this to a carbon dioxide .
[0005]
[Problem(s) to be Solved by the Invention] The amount of adsorption to the catalyst of a carbon monoxide is proportional also to the concentration. As mentioned above, on an electrode, although a reformer can be resembled and carbon monoxide concentration in fuel gas can be made low more, since the hydrogen in fuel gas is used in accordance with the flow of fuel gas, as for the downstream of the flow of fuel gas, carbon monoxide concentration becomes high relatively. Therefore, in the downstream of the flow of fuel gas, the amount of adsorption of a carbon monoxide increases and dissociation of the hydrogen by the catalytic reaction shown in (1) type is barred.
[0006]
$H_2 \rightarrow 2H_2+2e^-$ (1)
Consequently, in the downstream, the corrosion of the carbon of the electrode by the reaction shown in (2) types becomes easy to break out.
$C+2H_2O \rightarrow CO_2+4H^{++}4e^-$ (2)
The problem is the corrosion of an electrode progressing from the downstream of the fuel gas of an electrode surface as mentioned above, and reducing the life of a cell.
[0007] Made in order that this invention may solve this problem, that purpose is the downstream of fuel gas and is to offer the fuel electrode of the fuel cell which is not corroded with a carbon monoxide.
[0008]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the

catalyst bed formed so that it might continue throughout resulting [from the upstream of the fuel gas supplied to this electrode] in the downstream, and the sequential increment of the amount of support of the platinum particle used for a catalyst might be carried out gradually or the particle size of a platinum particle might become small gradual one by one is used for the fuel electrode of the fuel cell of this invention. Or using the catalyst which supported the platinum-ruthenium alloy, a catalyst bed is formed so that the content of a ruthenium may increase one by one gradually from the upstream of fuel gas to the downstream.

[0009]

[Function] To the carbon monoxide concentration which became high relatively by the downstream of the flow of fuel gas by constituting a fuel electrode as mentioned above, since the surface area of the platinum in the downstream of fuel gas is large, hydrogen becomes easy to stick to platinum. Moreover, since a carbon monoxide tends to stick to a ruthenium when using a platinum-ruthenium alloy for a catalyst, it is the downstream of the flow of fuel gas, and hydrogen comes to stick to platinum, so that a ruthenium content increases.

[0010] In any case, resistance [as opposed to a carbon monoxide in the downstream to which the carbon monoxide concentration in the fuel gas with which the fuel electrode by this invention is supplied becomes high] is high, and the life of a cell can be prolonged, without a reaction like corrosion of carbon occurring, since dissociation of hydrogen is fully performed.

[0011]

[Example] This invention is explained based on an example below. The electrode of a fuel cell consists of a carbon base material and a catalyst bed which combined with carbon black the catalyst which supported platinum or a platinum alloy by PTFE (PORETETORAFURORO ethylene). This invention constitutes the fuel electrode which has the catalyst bed to which the amount of platinum support of a platinum catalyst, platinum particle diameter, or the amount of rutheniums that is the alloy element of a platinum alloy catalyst was gradually changed about the each.

[0012] Catalyst 1cm3 after using ultrasonic gay NAIZA for the ion exchange water into which the surfactant went the specified quantity of the catalyst which supported example 1. platinum 10wt% to carbon black and distributing it to homogeneity A PTFE distribution solution (60% of concentration, specific gravity 1.5) which PTFE (PORETETORAFURORO ethylene) of 1g of hits mixes is added, it mixes further, and a catalyst / PTFE distribution solution is produced, and let this be dispersion liquid 1.

[0013] next, the catalyst which supported platinum 15wt% to carbon black -- using -- dispersion liquid 1 -- ** -- dispersion liquid 2 are produced by the same approach. Dispersion liquid 3, dispersion liquid 4, and dispersion liquid 5 are produced like the following using the catalyst which supported platinum 20wt% to carbon black, respectively, the catalyst which supported platinum 25wt% to carbon black, and the catalyst which supported platinum 30wt% to carbon black. At this time, the platinum particle size supported makes mostly the catalyst used for dispersion liquid 1 - dispersion liquid 5 an equal (for example, 30A), and it also makes the amount used this volume.

[0014] Subsequently, these have equal width of face toward the other end in order of dispersion liquid 1, dispersion liquid 2, dispersion liquid 3, dispersion liquid 4, and dispersion liquid 5 from the end of the porous carbon base material front face which gave a water-repellent finish by fluorine system resin beforehand, and it applies with the blade method or a spray method so that it may become this area. Drawing 1 is the mimetic diagram which showed the spreading field of dispersion liquid 1 - dispersion liquid 5, and looked at the spreading side of a carbon base material from the top. In drawing 1 , it means having applied dispersion liquid 1 - dispersion liquid 5 to the spreading field 1 - the spreading field 5. After drying the whole in this condition, it can calcinate at the temperature which PTFE fuses and the fuel electrode with which the catalyst bed was formed on the carbon base material can be obtained. Let this be a fuel electrode 1.

[0015] Although it calcinated at the temperature which PTFE fuses and the fuel electrode 2 was produced for the comparison here after applying and drying the same solution as dispersion liquid 1 with the blade method or a spray method to the porous carbon base material which carried out amount production 5 times and gave a water-repellent finish by fluorine system resin, this is equivalent to the fuel electrode currently used conventionally. Next, the cell was produced using these fuel electrodes 1 and a fuel electrode 2. A cell is constituted so that the side which applied

dispersion liquid 1 at this time, i.e., the direction of the spreading field 1 of drawing 1 , may turn into the upstream of fuel gas and the side which applied dispersion liquid 5, i.e., the direction of the spreading field 5 of drawing 1 , may turn into the downstream of fuel gas.
[0016] Drawing 2 is the diagram showing aging of the output characteristics of these cells. Curvilinear (b) which showed property change of the cell by which curvilinear (b) in drawing 2 has a fuel electrode 1, i.e., the fuel electrode which used the catalyst with a high platinum support rate for the downstream of the fuel gas in this invention, and was shown by the dotted line expresses property change of the cell which has a fuel electrode of the former for a fuel electrode 2, i.e., a comparison. It turns out that the direction of the cell which has the fuel electrode of this invention which used the catalyst with a high platinum support rate for the downstream of fuel gas from drawing 2 has little degradation of a property, and is maintaining long-term stability.
[0017] Moreover, as a result of disassembling the cell after operation and investigating the condition of an electrode, as for most fuel electrodes of this invention, corrosion is not accepted in a fuel electrode 2 to corrosion having been seen.
Example 2. particle size produces dispersion liquid 6 by the same approach as example 1. using the catalyst which supported the platinum particle which is 90A to carbon black. Dispersion liquid 7, dispersion liquid 8, dispersion liquid 9, and dispersion liquid 10 are produced using the catalyst which similarly supported the platinum particle whose particle size is 70A to carbon black, the catalyst which supported the platinum particle whose particle size is 50A to carbon black, the catalyst which supported the platinum particle whose particle size is 30A to carbon black, and the catalyst which supported the platinum particle whose particle size is 10A to carbon black, respectively. At this time, the amount of support of platinum makes mostly the catalyst used for dispersion liquid 6 - dispersion liquid 10 an equal (for example, 20%), and let the amount used be this volume.
[0018] Next, these have equal width of face toward the other end as well as the case of example 1. in order of dispersion liquid 6, dispersion liquid 7, dispersion liquid 8, dispersion liquid 9, and dispersion liquid 10 from the end of the porous carbon base material front face which gave a water-repellent finish by fluorine system resin beforehand, and it applies with the blade method or a spray method so that it may become this area. Since the spreading condition to a carbon base material is easily known if drawing 1 is referred to, illustration is excluded. And it can calcinate after desiccation at the temperature which PTFE fuses, and a fuel electrode 3 can be obtained.
[0019] The cell produced using a fuel electrode 3 makes the spreading field of the dispersion liquid 6 of a fuel electrode 3 the upstream of fuel gas, and it constitutes a cell so that it may become the downstream of fuel gas in the spreading field of dispersion liquid 10. The property of a cell is written together as a curve (Ha) to drawing 2 described previously. The cell which has the fuel electrode of this invention using the catalyst which supported the platinum particle with a small particle size to the downstream of fuel gas is almost the same as the case of the fuel electrode 1 [curvilinear (b)] stated by example 1., there is little degradation of a property compared with the fuel electrode 2 of the former [curvilinear (b)], and long-term stability is maintained so that drawing 2 may show.
[0020] Moreover, as a result of disassembling the cell after operation and investigating the condition of an electrode like example 1., corrosion is hardly accepted. As mentioned above, in example 1. and example 2., it is considered that the platinum surface area of the catalyst per electrode unit area also increases relatively as the carbon monoxide concentration in the fuel gas supplied to an electrode increases. That is, it is that of ** barred that hydrogen sticks to platinum with a carbon monoxide, and it is because hydrogen will become easy to adsorb if the surface area of platinum becomes large relatively.
[0021] The same dispersion liquid 11 as the dispersion liquid 1 in example 1. are produced using the catalyst which supported example 3. platinum 10wt% to carbon black. Next, dispersion liquid 12 are produced by the same approach as dispersion liquid 11 using the catalyst which supported the platinum 10wt%-ruthenium 0.7wt% alloy to carbon black. Hereafter, dispersion liquid 13, dispersion liquid 14, and dispersion liquid 15 are similarly produced using the catalyst which supported the platinum 10wt%-ruthenium 1.3wt% alloy to carbon black, the catalyst which supported the platinum 10wt%-ruthenium 2.6wt% alloy to carbon black, and the catalyst which supported the platinum 10wt%-ruthenium 5.2wt% alloy to carbon black, respectively. The amount of platinum of the

catalyst used for dispersion liquid 11 - dispersion liquid 15 is made to become equal at this time.
[0022] However, if the amount of rutheniums of a platinum 10wt%-ruthenium alloy exceeds 10wt (s)% in this case, since the property of a cell will fall, the amount of rutheniums must be made into a maximum of 10 wt%. Therefore, how to increase the amount of rutheniums may decide to consider as five steps, 2, 4, 6, 8, and 10wt%, suitably in the inside to 10wt%, without restricting above.
[0023] Subsequently, in example 1. and example 2., these have equal width of face toward the other end in order of dispersion liquid 11, dispersion liquid 12, dispersion liquid 13, dispersion liquid 14, and dispersion liquid 15 from the end of the porous carbon base material front face which gave a water-repellent finish by fluorine system resin beforehand, and similarly, it applies with the blade method or a spray method so that it may become this area. Since it understands easily if the spreading condition to a carbon base material refers to drawing 1 also in this case, illustration is excluded. And it calcinates after desiccation at the temperature which PTFE fuses, and a fuel electrode 4 is obtained.
[0024] Here, although the cell which used the fuel electrode 4 is produced, the spreading field of the dispersion liquid 11 of a fuel electrode 4 is made into the upstream of fuel gas, and a cell is constituted so that it may become the downstream of fuel gas in the spreading field of dispersion liquid 15. Although drawing 3 is the diagram showing aging of the output characteristics of the cell which imitated example 1. and example 2., and was produced using the fuel electrode 4 and curvilinear (d) shows it, it has re-**(ed) curvilinear (b) as a property of the cell using the fuel electrode 1 equivalent to the conventional fuel electrode already stated to drawing 3 at coincidence for the comparison.
[0025] According to drawing 3 , it turns out that the direction which used the fuel electrode using a platinum alloy catalyst with many rates which contain a ruthenium in the downstream of fuel gas has little property degradation of a cell, and maintains long-term stability. As a result of disassembling the cell after operation also in this case and investigating the condition of an electrode, corrosion is hardly accepted in the fuel electrode by this invention. Since a carbon monoxide tends to stick to a ruthenium, the process in which fuel gas passed along a fuel electrode increased the amount of rutheniums in stairway by example 3., and it is the downstream of the flow of gas, and it is because hydrogen comes to stick to platinum, so that a ruthenium increases.
[0026] Although the fuel electrode of the fuel cell of this invention was explained as a configuration which has the catalyst bed which changed the amount of platinum support of a platinum catalyst, platinum particle diameter, or the amount of rutheniums that is the alloy element of a platinum alloy catalyst to division into equal parts about the each in five steps as stated above Since the most desirable condition gives continuous inclination, applying the method of this change to the downstream from the upstream of fuel gas, using five steps of change [****] as the fuel electrode subdivided further is also considered, this is decided according to the actual condition and that of **** is good.
[0027]
[Effect of the Invention] The fuel gas which flows the fuel electrode of a fuel cell contains the carbon monoxide, and from the upstream in an electrode, since the direction of the downstream becomes high, this carbon monoxide concentration As opposed to the problem of spoiling the property of a lifting cell for the corrosion of an electrode since the hydrogen of fuel gas stops being able to stick to the platinum of an electrode catalyst easily in the downstream the fuel electrode of this invention The amount of support of the platinum particle of an electrode catalyst is gradually increased one by one from the upstream of fuel gas to the downstream. Or making the particle diameter of a platinum particle small gradual one by one from the upstream of fuel gas to the downstream etc. corresponds to the location of the fuel electrode with which fuel gas flows. When making it become large in the surface area of a platinum particle gradually and using a platinum-ruthenium alloy for an electrode catalyst toward the upstream to the downstream By making [many] the content of a ruthenium gradually from the upstream of fuel gas to the downstream, dissociation of hydrogen can fully be performed, it is made hard to happen the corrosion of an electrode, consequently the downstream of fuel gas can also prevent degradation of a cell property, and can prolong a battery life.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The mimetic diagram showing the spreading condition to the substrate of dispersion liquid with which the amounts of platinum support in this invention differ
[Drawing 2] The diagram having shown the cell property of having the electrode of this invention, by the comparison with the conventional cell property
[Drawing 3] The diagram having shown the cell property of having the electrode of another this invention with drawing 2 by the comparison with the conventional cell property
[Description of Notations]
Nothing

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(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平7－85874

(43)公開日　平成７年(1995)３月31日

(51)Int.Cl.[6]		識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｈ０１Ｍ	4/86	Ｍ			
	4/88	Ｋ			
	4/92				

審査請求　未請求　請求項の数５　ＯＬ　（全 ５ 頁）

(21)出願番号　特願平5－229343

(22)出願日　平成５年(1993)９月16日

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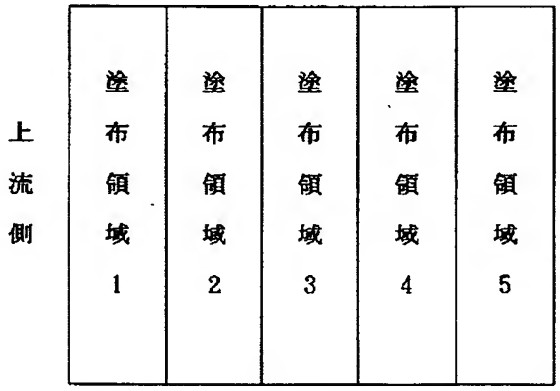
(54)【発明の名称】　燃料電池の燃料電極

(57)【要約】

【目的】一酸化炭素を含む燃料ガスの下流側で、電極が一酸化炭素による被毒を受けないようにする。

【構成】燃料ガスの上流側から下流側にかけて、触媒の白金微粒子の担持量を段階的に増加させ、または白金微粒子の粒径が段階的に小さくなるように形成した触媒層を用い、もしくは、白金－ルテニウム合金触媒では、燃料ガスの上流側から下流側まで、ルテニウムの含有量が段階的に多くなるように触媒層を形成することにより、燃料ガスの下流側で相対的に一酸化炭素濃度が高くなっても、白金に燃料ガス中の水素が吸着しやすくなり、電極の腐食を起こすことなく、電池の寿命を長期間安定させることができる。



【特許請求の範囲】

【請求項１】カーボン基材と、カーボンブラックに白金微粒子を担持した触媒を有する触媒層とからなる燃料電池の燃料電極であって、この電極に供給される燃料ガスの上流側から下流側に至る全域に亘って、電極単位面積当たりの白金微粒子の表面積を段階的に順次増加させた触媒層を形成することを特徴とする燃料電池の燃料電極。

【請求項２】請求項１記載の燃料電極において、白金微粒子の表面積の増加はその担持量を段階的に増すことにより行なうことを特徴とする燃料電池の燃料電極。

【請求項３】請求項１記載の燃料電極において、白金微粒子の表面積の増加はその粒径を段階的に小さくすることにより行なうことを特徴とする燃料電池の燃料電極。

【請求項４】カーボン基材と、カーボンブラックに白金合金微粒子を担持した触媒を有する触媒層とからなる燃料電池の燃料電極であって、この電極に供給される燃料ガスの上流側から下流側に至る全域に亘って、白金と合金化する元素の含有量を段階的に順次増加させた触媒層を形成することを特徴とする燃料電池の燃料電極。

【請求項５】請求項４記載の燃料電極において、白金と合金化する元素としてルテニウムを用いることを特徴とする燃料電池の燃料電極。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は白金系の触媒を用いた燃料電池の燃料電極に関する。

【０００２】

【従来の技術】燃料電池の燃料ガスとして水素を用いることは、経済的に不利であることから、通常、天然ガスなどの炭化水素系の原燃料を、水素分に富んだガスに改質したものを燃料ガスとして使用している。このような改質ガスには、水素ガスのほかに二酸化炭素もしくは一酸化炭素などの不純物が含まれている。

【０００３】一方、比較的低温で運転される燐酸形燃料電池や固体高分子形燃料電池では、白金黒やカーボン担体に、白金または白金合金を担持した白金触媒または白金合金触媒が電極に使用されている。これらの電極触媒は、燃料ガス中に一酸化炭素が含有されていると、この一酸化炭素が吸着して燃料電極における分極が大きくなり、その結果燃料電池の発生電圧が低下し、特に、燃料電池の運転温度が低い場合は、発生電圧が極端に低下することが知られている。

【０００４】そこで、現状は原燃料を水素分に富んだガスに改質する改質装置に、一酸化炭素を除去するか、またはこれを二酸化炭素に酸化するなどの機能を持たせることにより、燃料ガス中の一酸化炭素濃度を、電池の性能に影響を及ぼさない程度に保つようにしており、また、電池本体では燃料電極に用いる触媒として、一酸化炭素の被毒を受け難い白金－ルテニウム合金触媒などを

用いることが行なわれている。

【０００５】

【発明が解決しようとする課題】一酸化炭素の触媒への吸着量はその濃度にも比例する。前述のように、改質装置ににより燃料ガス中の一酸化炭素濃度を低くすることはできるが、電極上では、燃料ガスの流れに沿って燃料ガス中の水素が使われていくために、燃料ガスの流れの下流側は、相対的に一酸化炭素濃度が高くなる。したがって、燃料ガスの流れの下流側では、一酸化炭素の吸着量が多くなり、（１）式に示す触媒反応による水素の解離が妨げられる。

【０００６】

$H_2 \rightarrow 2H^2 + 2e^-$ （１）

その結果、下流側では（２）式に示す反応による電極のカーボンの腐食が起きやすくなる。

$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ （２）

問題は、以上のようにして電極面の燃料ガスの下流側から電極の腐食が進み、電池の寿命を低下させることである。

【０００７】本発明はこの問題を解決するためになされたものであり、その目的は、燃料ガスの下流側で、一酸化炭素によって腐食されることのない燃料電池の燃料電極を提供することにある。

【０００８】

【課題を解決するための手段】上記の課題を解決するために、本発明の燃料電池の燃料電極は、この電極に供給される燃料ガスの上流側から下流側に至る全域に亘って、触媒に用いる白金微粒子の担持量を、段階的に順次増加させ、または白金微粒子の粒径が段階的に順次小さくなるように形成した触媒層を用いる。もしくは、白金－ルテニウム合金を担持した触媒を用い、燃料ガスの上流側から下流側まで、ルテニウムの含有量が段階的に順次多くなるように触媒層を形成する。

【０００９】

【作用】燃料電極を上述のように構成することにより、燃料ガスの流れの下流側で相対的に高くなった一酸化炭素濃度に対して、燃料ガスの下流側における白金の表面積が大きいので、白金に水素が吸着しやすくなる。また、触媒に白金－ルテニウム合金を用いるときは、一酸化炭素がルテニウムに吸着しやすいから、燃料ガスの流れの下流側で、ルテニウム含有量が多くなる程、白金に水素が吸着するようになる。

【００１０】いずれの場合も、本発明による燃料電極は、供給される燃料ガス中の一酸化炭素濃度が高くなる下流側でも、一酸化炭素に対する耐性が高く、水素の解離が十分に行なわれるので、カーボンの腐食のような反応が起こることなく、電池の寿命を延ばすことができる。

【００１１】

【実施例】以下本発明を実施例に基づき説明する。燃料

電池の電極は、カーボン基材と、カーボンブラックに白金または白金合金を担持した触媒をＰＴＦＥ（ポレテトラフロロエチレン）で結合した触媒層とからなる。本発明は、白金触媒の白金担持量、白金粒子径、または白金合金触媒の合金元素であるルテニウム量を、その各々について段階的に変化させた触媒層を有する燃料電極を構成したものである。

【００１２】実施例１．白金１０ｗｔ％をカーボンブラックに担持した触媒の所定量を、界面活性剤の入ったイオン交換水に、超音波ホモナイザーを用いて均一に分散させた後、触媒１ｃｍ^3 当たり１ｇのＰＴＦＥ（ポレテトラフロロエチレン）が混合するようなＰＴＦＥ分散溶液（濃度６０％，比重１．５）を加え、さらに混合して、触媒／ＰＴＦＥ分散溶液を作製し、これを分散液１とする。

【００１３】次に白金１５ｗｔ％をカーボンブラックに担持した触媒を用いて、分散液１とと同様の方法で分散液２を作製する。以下同様にして、それぞれ白金２０ｗｔ％をカーボンブラックに担持した触媒，白金２５ｗｔ％をカーボンブラックに担持した触媒，および白金３０ｗｔ％をカーボンブラックに担持した触媒を用いて、分散液３，分散液４，分散液５を作製する。このとき、分散液１～分散液５に使用する触媒は、担持される白金粒径がほぼ等しいもの（例えば３０Å）とし、使用量も同体積とする。

【００１４】次いで、あらかじめ弗素系樹脂で撥水処理を施した多孔性カーボン基材表面の一端から他端に向かって、分散液１，分散液２，分散液３，分散液４，分散液５の順に、これらが等しい幅を有し、同面積となるように、ブレード法もしくはスプレー法で塗布する。図１は分散液１～分散液５の塗布領域を示し、カーボン基材の塗布面を上から見た模式図である。図１において、塗布領域１～塗布領域５に分散液１～分散液５を塗布したことを表わしている。この状態で全体を乾燥した後、ＰＴＦＥが溶融する温度で焼成し、カーボン基材上に触媒層の形成された燃料電極を得ることができる。これを燃料極１とする。

【００１５】ここで比較のために、分散液１と同じ溶液をその５倍量作製し、弗素系樹脂で撥水処理を施した多孔性カーボン基材に、ブレード法もしくはスプレー法で塗布し乾燥した後、ＰＴＦＥが溶融する温度で焼成し、燃料極２を作製したが、これは従来使用されている燃料電極に相当するものである。次に、これら燃料極１、燃料極２を用いて電池を作製した。このとき分散液１を塗布した側、即ち図１の塗布領域１の方が燃料ガスの上流側となり、分散液５を塗布した側、即ち図１の塗布領域５の方が燃料ガスの下流側となるように、電池を構成する。

【００１６】図２は、これら電池の出力特性の経時変化を示す線図である。図２中の曲線（イ）が燃料極１、即ち本発明における燃料ガスの下流側に白金担持割合の高い触媒を用いた燃料電極を有する電池の特性変化を示し、点線で示した曲線（ロ）が燃料極２、即ち比較のための従来相当の燃料電極を有する電池の特性変化を表わしている。図２から、燃料ガスの下流側に白金担持割合の高い触媒を用いた本発明の燃料電極を有する電池の方が、特性の劣化が少なく、長期間安定性を持続していることがわかる。

【００１７】また、運転後の電池を分解して電極の状態を調べた結果、燃料極２には腐食が見られたのに対し、本発明の燃料電極は殆ど腐食が認められない。

実施例２．粒径が９０Åの白金粒子をカーボンブラックに担持した触媒を用い、実施例１．と同様の方法で分散液６を作製する。同様にして、粒径が７０Åの白金粒子をカーボンブラックに担持した触媒，粒径が５０Åの白金粒子をカーボンブラックに担持した触媒，粒径が３０Åの白金粒子をカーボンブラックに担持した触媒，粒径が１０Åの白金粒子をカーボンブラックに担持した触媒を用いて、それぞれ分散液７，分散液８，分散液９，分散液１０を作製する。このとき、分散液６～分散液１０に用いる触媒は、白金の担持量がほぼ等しいもの（例えば２０％）とし、使用量は同体積とする。

【００１８】次に、実施例１．の場合と同じく、あらかじめ弗素系樹脂で撥水処理を施した多孔性カーボン基材表面の一端から他端に向かって、分散液６，分散液７，分散液８，分散液９，分散液１０の順に、これらが等しい幅を有し、同面積となるように、ブレード法もしくはスプレー法で塗布する。カーボン基材への塗布状態は、図１を参照すれば容易にわかるので図示は省く。そして乾燥後、ＰＴＦＥが溶融する温度で焼成し、燃料極３を得ることができる。

【００１９】燃料極３を用いて作製する電池は、燃料極３の分散液６の塗布領域の方を燃料ガスの上流側とし、分散液１０の塗布領域の方を燃料ガスの下流側となるように、電池を構成する。電池の特性は、先に述べた図２に曲線（ハ）として併記してある。図２からわかるように、燃料ガスの下流側に粒径の小さい白金微粒子を担持した触媒を用いた本発明の燃料電極を有する電池は、実施例１．で述べた燃料極１［曲線（イ）］の場合と殆ど同じであり、従来相当の燃料極２［曲線（ロ）］に比べて特性の劣化が少なく、長期間安定性を持続している。

【００２０】また、実施例１．と同様、運転後の電池を分解して電極の状態を調べた結果、殆ど腐食が認められない。以上、実施例１．，実施例２．では、電極に供給される燃料ガス中の一酸化炭素濃度が増すに従って、電極単位面積当たりの触媒の白金表面積も相対的に増すように考慮したものである。即ち、一酸化炭素によって白金に水素が吸着するのが妨げられるので、白金の表面積が相対的に大きくなれば、水素が吸着しやすくなるからである。

【００２１】実施例３．白金１０ｗｔ％をカーボンブラックに担持した触媒を用い、実施例１．における分散液１と同じ分散液１１を作製する。次に、白金１０ｗｔ％ールテニウム０．７ｗｔ％合金をカーボンブラックに担持した触媒を用い、分散液１１と同じ方法で分散液１２を作製する。以下、同様に、白金１０ｗｔ％ールテニウム１．３ｗｔ％合金をカーボンブラックに担持した触媒，白金１０ｗｔ％ールテニウム２．６ｗｔ％合金をカーボンブラックに担持した触媒，白金１０ｗｔ％ールテニウム５．２ｗｔ％合金をカーボンブラックに担持した触媒を用いて、それぞれ分散液１３，分散液１４，分散液１５を作製する。このとき、分散液１１～分散液１５に用いる触媒の白金量を等しくなるようにする。

【００２２】但し、この場合、白金１０ｗｔ％ールテニウム合金のルテニウム量が１０ｗｔ％を超えると、電池の特性が低下するので、ルテニウム量は最大１０ｗｔ％としなければならない。したがって、ルテニウム量の増やし方は、上記に限ることなく、１０ｗｔ％までの内で、例えば２，４，６，８，１０ｗｔ％の５段階とするなど、適当に決めてもよい。

【００２３】次いで、実施例１．，実施例２．における と同様に、あらかじめ弗素系樹脂で撥水処理を施した多孔性カーボン基材表面の一端から他端に向かって、分散液１１，分散液１２，分散液１３，分散液１４，分散液１５の順に、これらが等しい幅を有し、同面積となるように、ブレード法もしくはスプレー法で塗布する。この場合も、カーボン基材への塗布状態は、図１を参照すれば容易にわかるので図示は省く。そして乾燥後、ＰＴＦＥが溶融する温度で焼成し、燃料極４が得られる。

【００２４】ここでも、燃料極４を用いた電池を作製するが、燃料極４の分散液１１の塗布領域の方を燃料ガスの上流側とし、分散液１５の塗布領域の方を燃料ガスの下流側となるように、電池を構成する。図３は、実施例１．，実施例２．に倣って、燃料極４を用いて作製した電池の出力特性の経時変化を示す線図であり、曲線（ニ）で示しているが、同時に図３には、比較のために、既に述べた従来の燃料電極に相当する燃料極１を用いた電池の特性として、曲線（ロ）を再掲してある。

【００２５】図３によれば、燃料ガスの下流側に、ルテニウムを含む割合の多い白金合金触媒を用いた燃料電極を用いた方が、電池の特性劣化が少なく、長期間安定性を持続することがわかる。この場合も、運転後の電池を分解して電極の状態を調べた結果、本発明による燃料電極には殆ど腐食が認められない。実施例３．でルテニウム量を階段的に増やしたのは、一酸化炭素がルテニウムに吸着しやすいので、燃料ガスが燃料電極を通る過程で、ガスの流れの下流側で、ルテニウムが多くなる程、白金に水素が吸着するようになるからである。

【００２６】以上述べてきたように、本発明の燃料電池の燃料電極は、白金触媒の白金担持量、白金粒子径、または白金合金触媒の合金元素であるルテニウム量を、その各々について、例えば等分に５段階に変化させた触媒層を有する構成として説明したが、この変化のしかたは、燃料ガスの上流側から下流側にかけて、連続的な勾配を持たせるのが、最も望ましい状態であるから、等分な５段階の変化をさらに細分化した燃料電極とすることも考えられ、このことは実状に応じて決めれるのがよい。

【００２７】

【発明の効果】燃料電池の燃料電極を流れる燃料ガスは、一酸化炭素を含んでおり、この一酸化炭素濃度が電極内の上流側より下流側の方が高くなるので、下流側では燃料ガスの水素が電極触媒の白金に吸着し難くなることから、電極の腐食を起こし電池の特性を損なうという問題に対して、本発明の燃料電極は、電極触媒の白金粒子の担持量を、燃料ガスの上流側から下流側まで段階的に順次増やし、または白金粒子の粒子径を燃料ガスの上流側から下流側まで段階的に順次小さくするなど、燃料ガスの流れる燃料電極の場所に対応して、上流側から下流側に向かって、段階的に白金粒子の表面積か大きくなるようにし、また、電極触媒に白金ールテニウム合金を用いる場合は、ルテニウムの含有量を燃料ガスの上流側から下流側まで段階的に多くすることにより、燃料ガスの下流側でも水素の解離が十分に行なわれ、電極の腐食を起こり難くしており、その結果、電池特性の劣化を防ぎ、電池寿命を延ばすことができる。

【図面の簡単な説明】

【図１】本発明における白金担持量の異なる分散液の基板への塗布状態を示す模式図

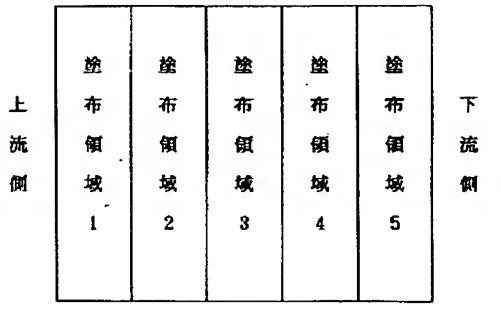
【図２】本発明の電極を有する電池特性を従来の電池特性との比較で示した線図

【図３】図２とは別の本発明の電極を有する電池特性を従来の電池特性との比較で示した線図

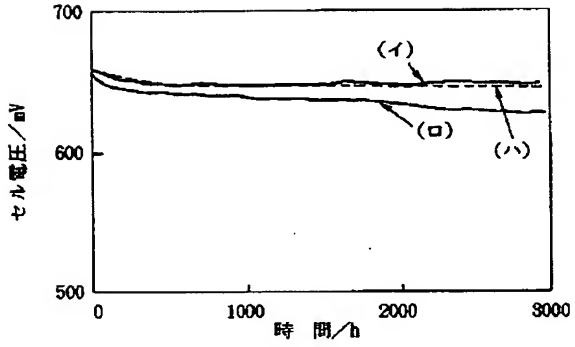
【符号の説明】

なし

【図１】



【図２】



【図３】